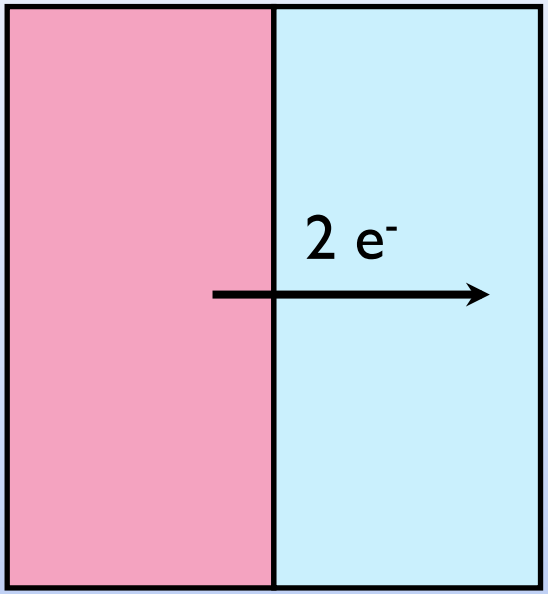
Today

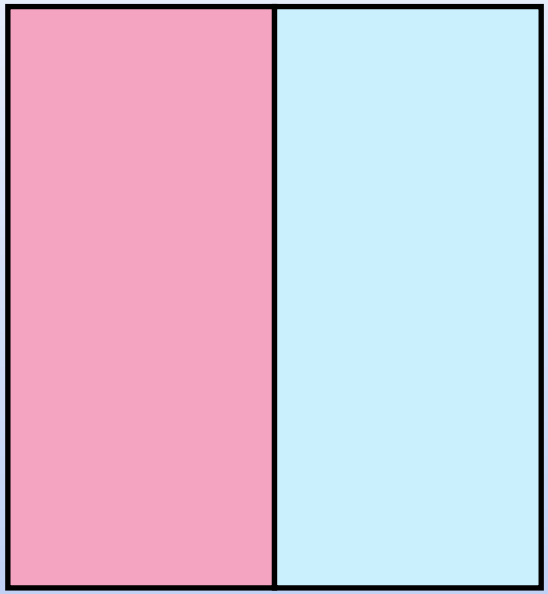
Galvanic Cells

Spontaneous Electrochemistry

Electrons have a lower free energy in Zn^{2+} (and Cu) than Cu^{2+} (and Zn)



Zn Cu^{2+}



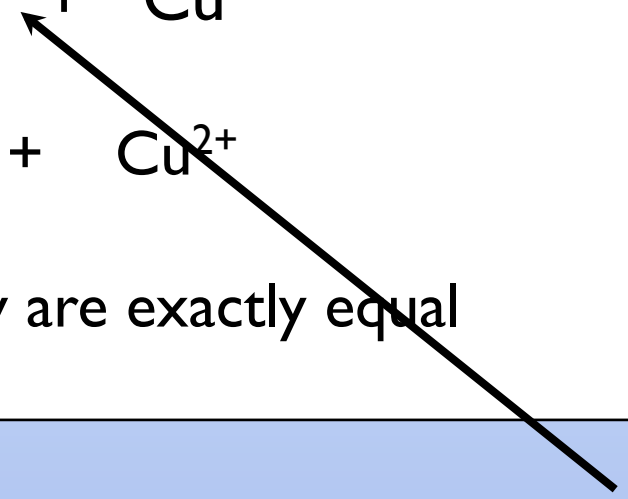
Zn^{2+} Cu

Which has the lower Standard Gibb's free energy?

A. Zn^{2+} + Cu

B. Zn + Cu^{2+}

C. They are exactly equal



The reaction will proceed spontaneously to the lowest free energy side

A moment to think again about Free Energy and Standard Free Energy

ΔG

Difference in Free Energy between reactants and product under the current conditions (depends on the **concentrations** of the reactants and products)

The concentration will change until $\Delta G = 0$

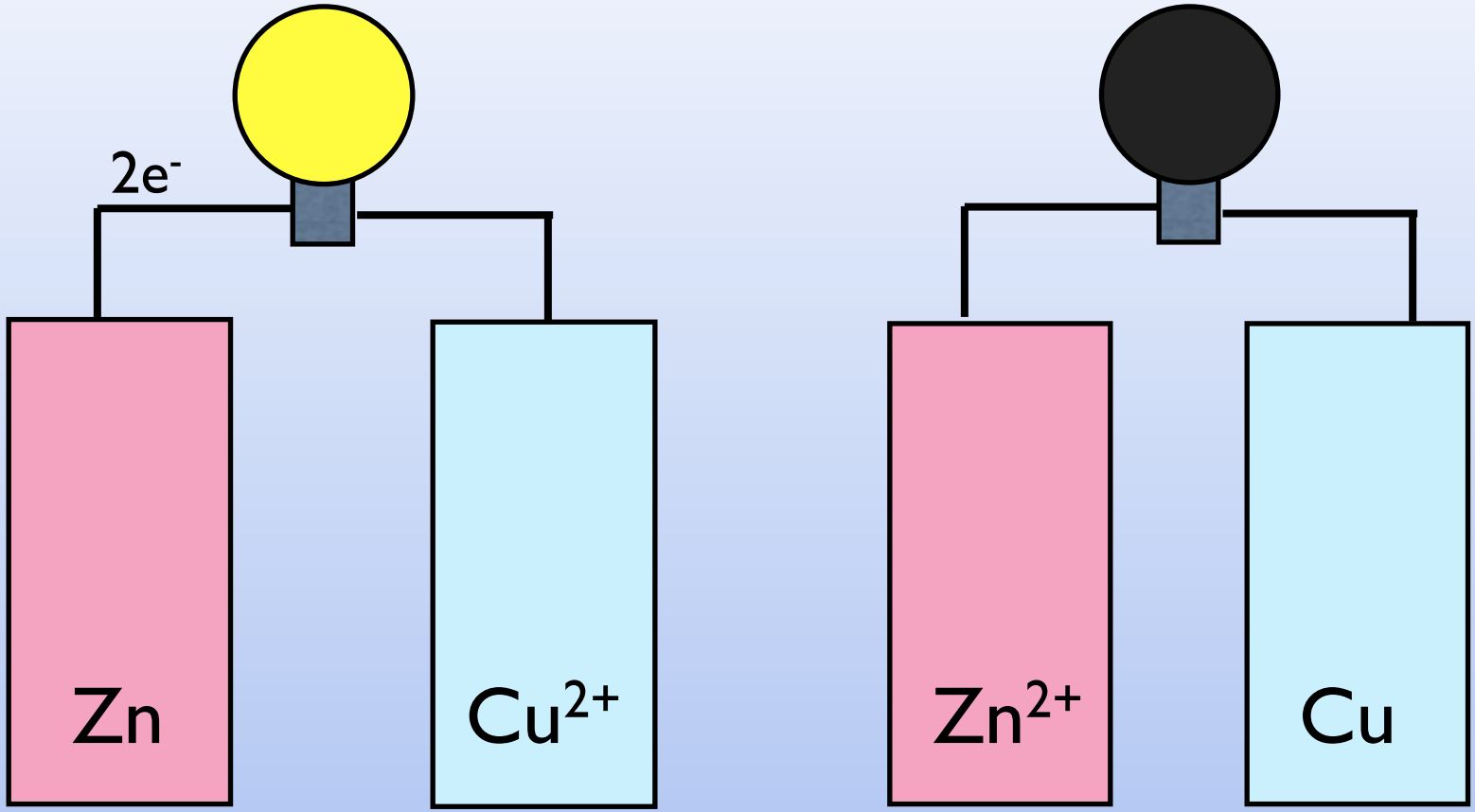
ΔG°

Difference in Free Energy between reactants and product under standard conditions

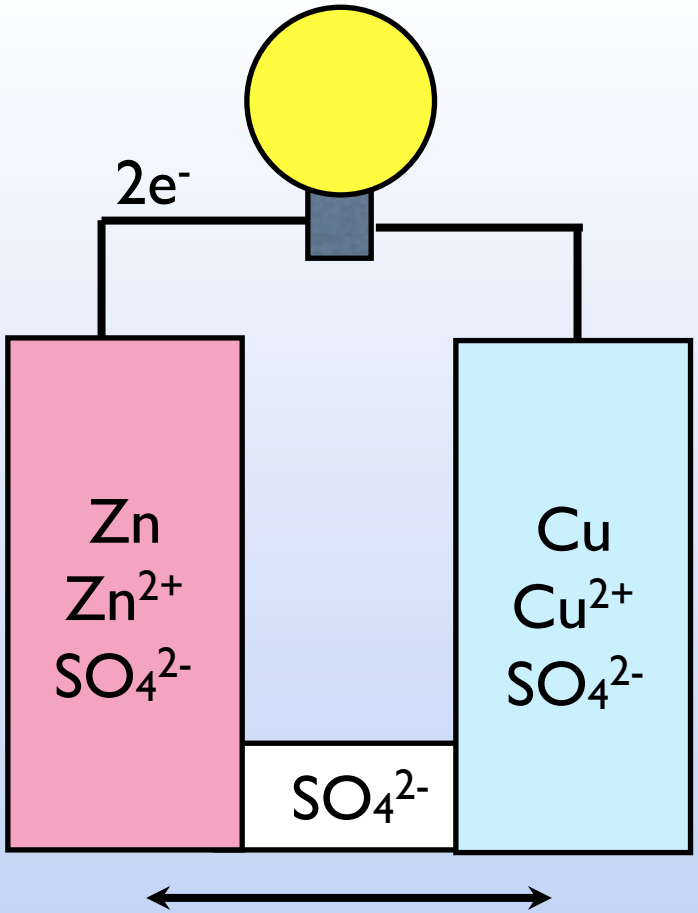
standard conditions are **1 M for all aqueous species**

or 1 atm pressure for all gases

Last time, we look at this idea
Use a wire to connect the two sides
and have e- flow in an external circuit

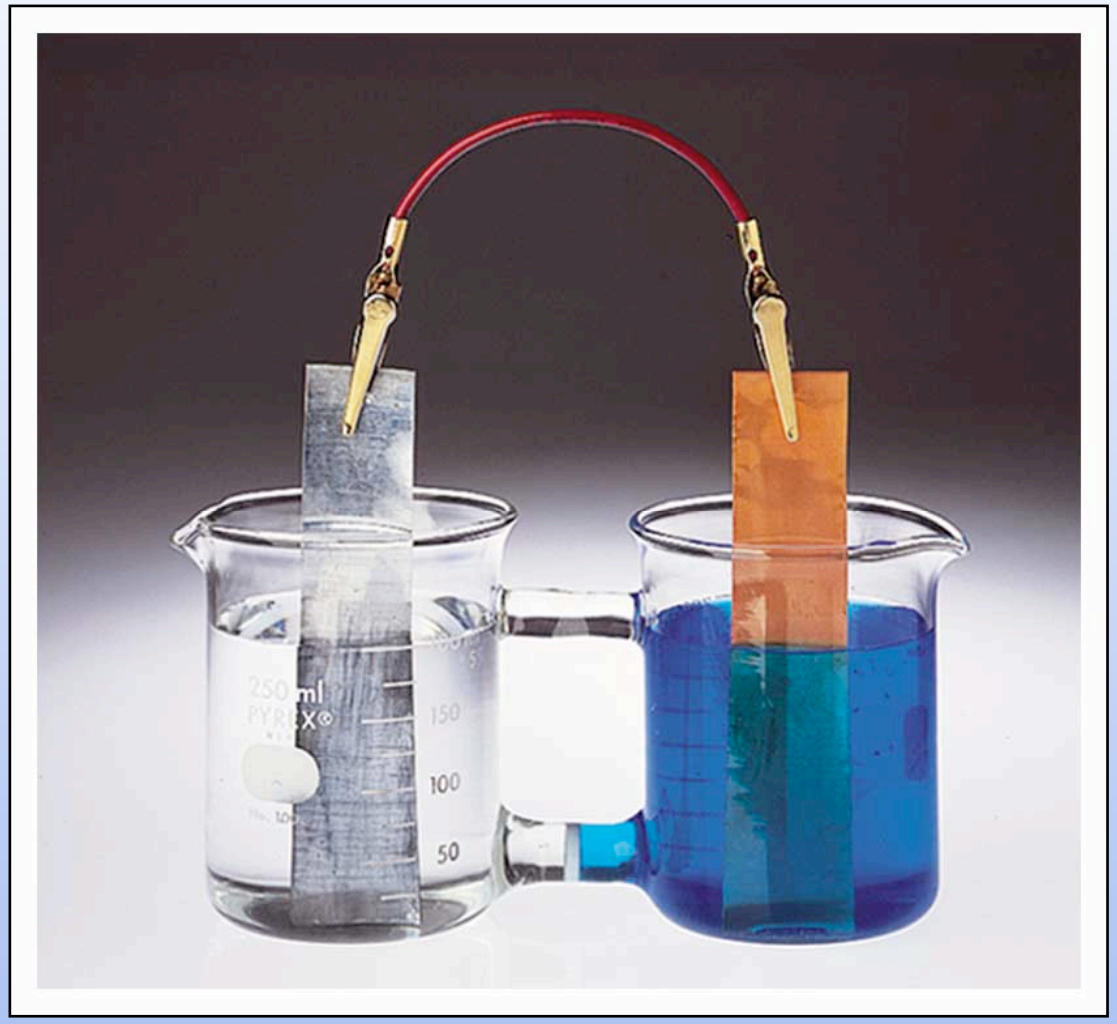


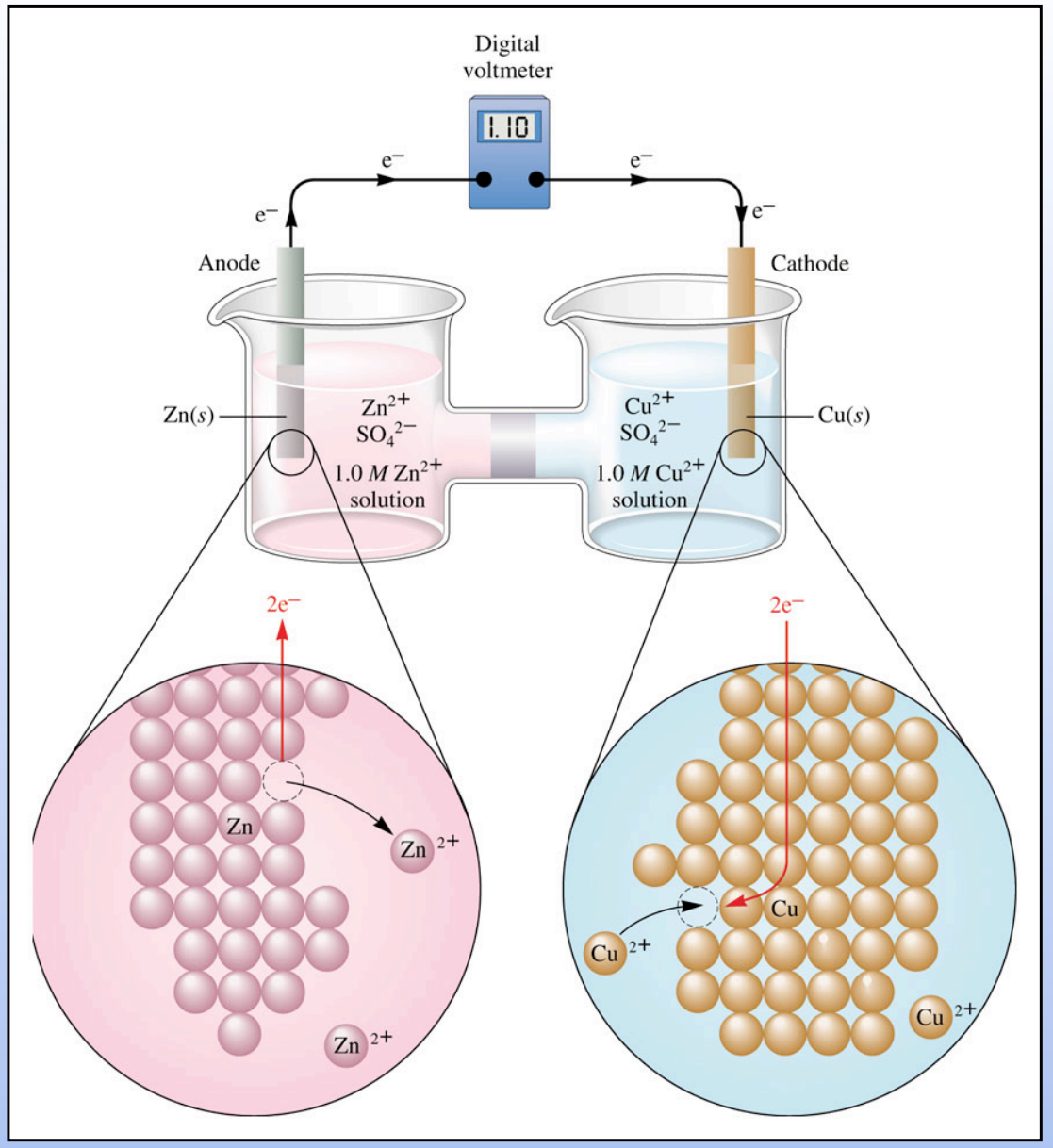
Problem, one side is getting more positive
one side is getting more negative.
We need to keep each side neutral



Add a connection that let's a "counter" ion move between the two sides

As the reaction proceeds Zn is oxidized into Zn^{2+}
Cu^{2+} is reduced into Cu
note I have two solid pieces of metal (electrodes) connected to the wire



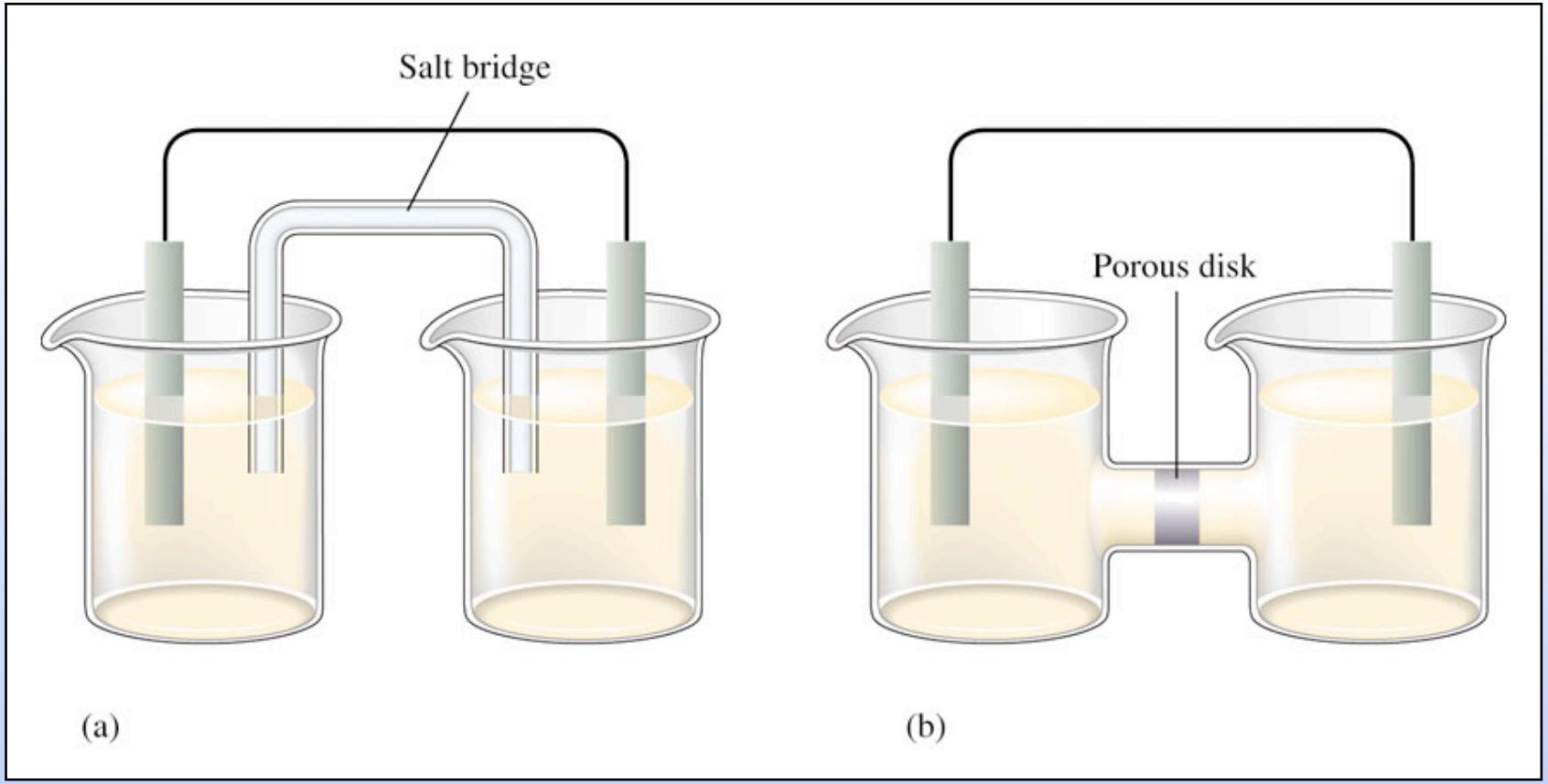


Oxidation

$Zn \rightarrow Zn^{2+} + 2\ e^-$

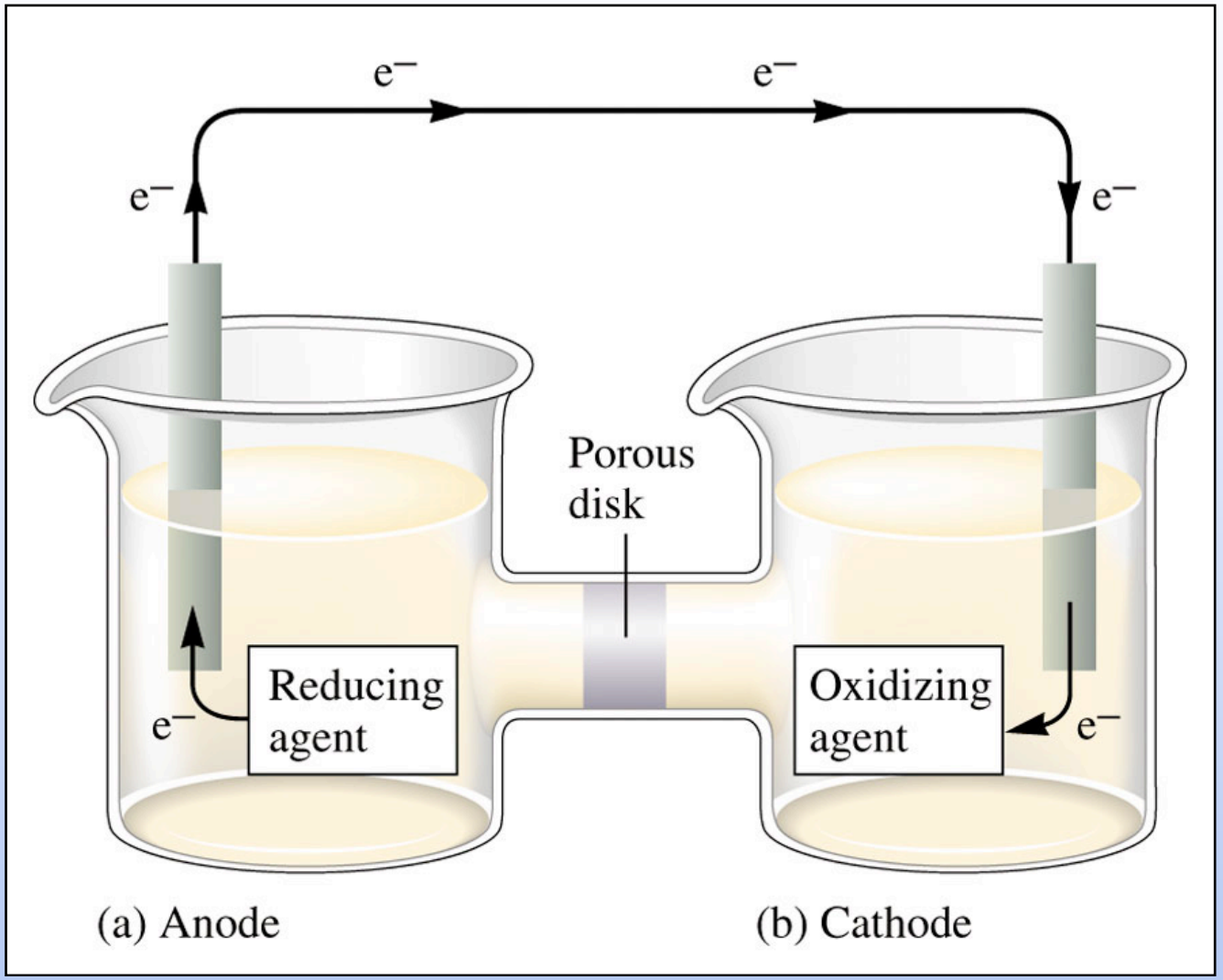
Reduction

$Cu^{2+} + 2e^- \rightarrow Cu$



Salt Bridge or Porous Disk allow ions to flow back and forth between the two beakers.

As e^- move from one side to the other, counter anions move the opposite direction



Anode.
Oxidation
reaction

Cathode.
Reduction
Reaction

How will I ever remember?

AN OX and RED CAT

ANode REDuction
OXidation CAThode

Cathode Ray Tube
Shoots out electrons

Alternatively just remember it!

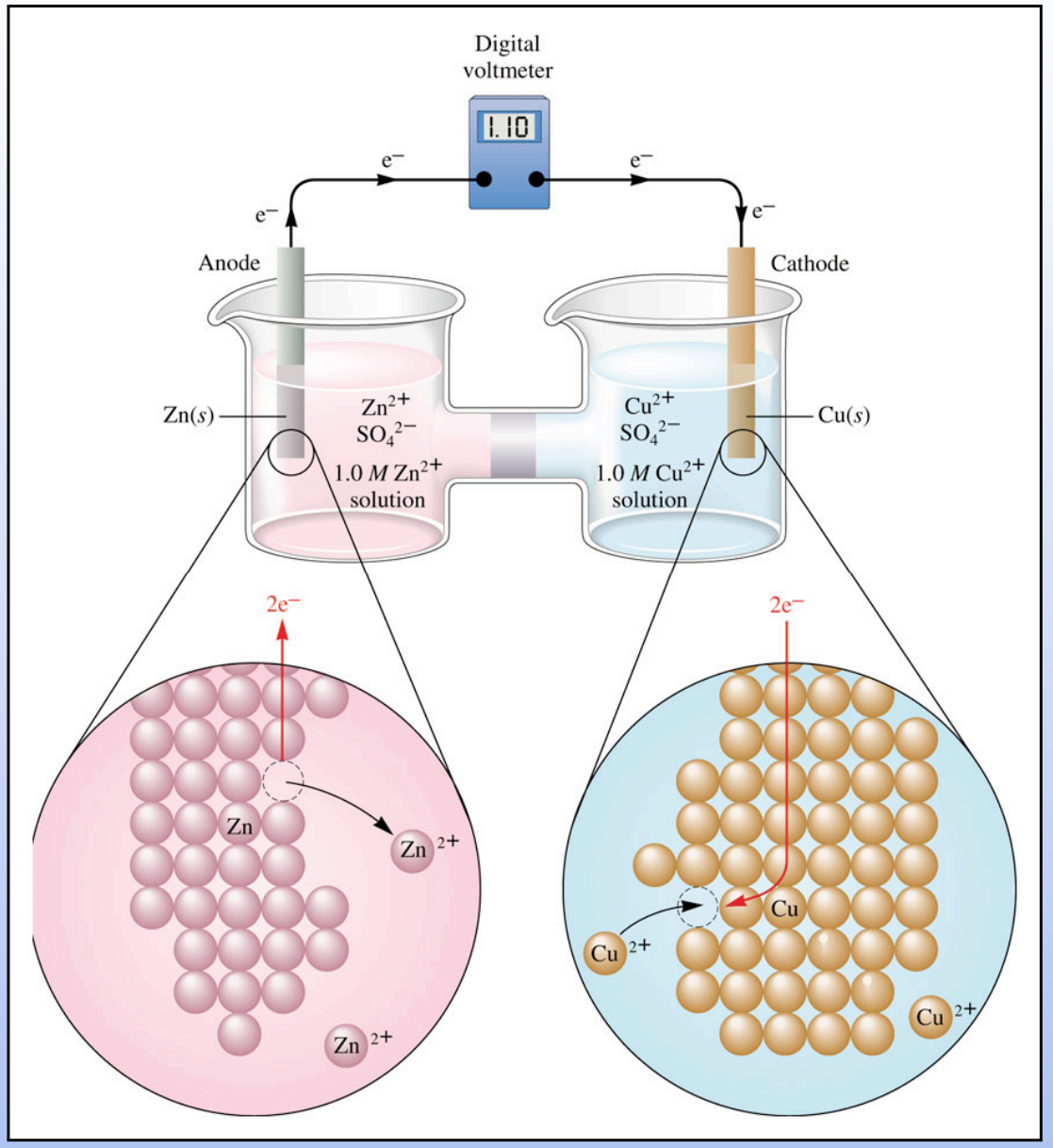
In our reaction of Zn goes to Zn^{2+}
and Cu^{2+} goes to Cu
What is the cathode?

A. The Cu strip

B. The Zn strip

C. neither

Reduction at the cathode.
Cu^{2+} is reduced to Cu



Oxidation

$Zn \rightarrow Zn^{2+} + 2\ e^-$

Reduction

$Cu^{2+} \rightarrow Cu + 2\ e^-$

To write this out we develop a short hand

symbol for the short hand

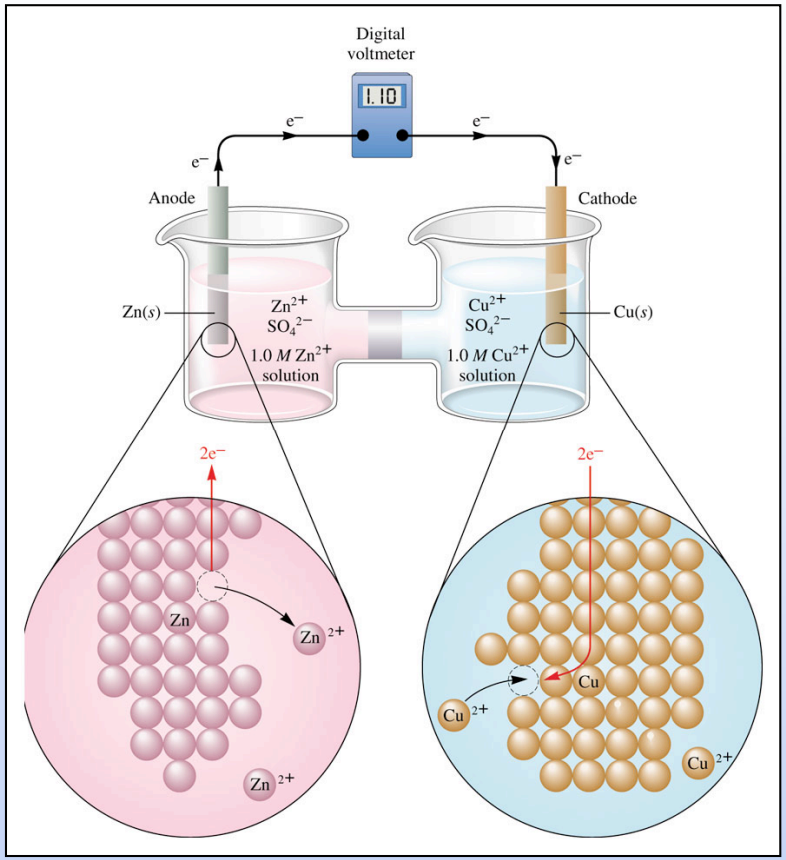
|| = "salt bridge" this divides the cell into to halves
| = show the different compounds of each 1/2 reaction

By convention the anode is always on the "left"

So for the cell we just had

We can write this as

<Zn|Zn^{2+}||Cu^{2+}|Cu>



if we knew the
concentrations of the ions

<Zn|Zn^{2+}(1 M) ||Cu^{2+}(1 M) |Cu>

Other reactions

One half is
Oxidation (Anode) Ag goes to Ag+

Reduction (Cathode) Fe^{3+} goes to Fe^{2+}

$< Ag \mid Ag^{+} \parallel Fe^{3+} \mid Fe^{2+} >$

but we would like this to represent the actual cell
I cannot hook a wire up to Fe^{2+}. I need an electrode in the solution. Let's say I use a Pt electrode

$< Ag \mid Ag^{+} \parallel Fe^{3+} \mid Fe^{2+} \mid Pt >$

Two "kinds" of electrochemical cells

Galvanic (Voltaic)
Reaction is spontaneous
we can use these to make a battery

Electrolytic
Reaction is not spontaneous
we have to input work to get these reactions to proceed

Formulas for the quiz

$K_w = K_aK_b = 10^{-14}$ (25°C)

$[H^+] = (K_aC_{HA})^{0.5}$ $\quad$ $[OH^-] = (K_bC_B)^{0.5}$

$[H^+] = (K_{a1}K_{a2})^{0.5}$ $\quad$ $[OH^-] = (K_{b1}K_{b2})^{0.5}$

$[H^+] = C_A$ $\quad$ $[OH^-] = C_B$

$[H^+] = K_A(C_a/C_b)$ $\quad$ $[OH^-] = K_B(C_b/C_a)$

$$[H^+]^2 - [H^+]C_a - K_w = 0$$

$$[OH^-]^2 - [OH^-]C_b - K_w = 0$$